In the limit of high mass transfer rates from the surface of the particle, there is set up a situation in which mass transfer is controlled through a thin 'boundary layer' of steep concentration gradients very near the particle surface.

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A note on the inverse problem of radial diffusion in a semi-infinite porous medium

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INTRODUCTION

CONTAMINANT transport in subsurface repositories and related systems is an issue of growing concern [1, 2]. The interest arises in part because of the need to assess the probability of release of contaminants and also to determine their rate of transport.

Vapors from a concentrated source are transported by molecular diffusion if the source pressure and the pore pressure of the surrounding porous medium are equal. Otherwise, pressure-driven flow contributes to the rate of transport. In the former case, only the porosity and mass diffusivity affect the rate of transport. Porosity is accurately determined from laboratory tests performed on samples of the medium. However, accurate estimates of diffusivity are found only through *in situ* methods for at least two reasons. First, preferential paths for diffusion that exist in the unstressed medium may not exist under *in situ* conditions where stresses can be large. Secondly, it is very difficult to replicate *in situ* moisture conditions in the laboratory.

Recent studies to determine thermal and mass transport molecular properties have focused on laboratory tests and theoretical analyses rather than *in situ* tests to calculate properties from global measurements [3–6]. These include laboratory tests to determine thermal diffusivity of gases in fibrous insulation materials [3], and mass diffusion coefficients for binary gas flow in closed-cell insulation systems [4]. One type of *in situ* test to determine effective mass diffusivity in homogeneous porous media consists of isolating an initially known concentration of gas in a well installed in the medium. The time-history of gas concentration is monitored and the data used in an appropriate model of mass diffusion from which mass diffusivity is estimated.

The solution for gas diffusion in a semi-infinite porous medium, with particular attention to solving the inverse problem for *in situ* effective mass diffusivity, is the focus of this note.

FORMULATION

An initially known concentration of gas is isolated in a circular well of radius R in a semi-infinite, isotropic, homogeneous porous medium of uniform porosity, ϕ, and effective mass diffusivity, D_{eff}. As time progresses, concentration of the isolated gas decreases because of diffusion of mass into the medium. We wish to determine the effective mass diffusivity for the medium of known porosity by measuring the time-history of this concentration.

If the length of the isolated gas is much larger than the penetration depth of the diffused mass, the diffusion process can be approximated as only radial. The diffusion equation for the scaled concentration, C (ratio of molar concentration and initial concentration of the isolated gas), in the porous medium is

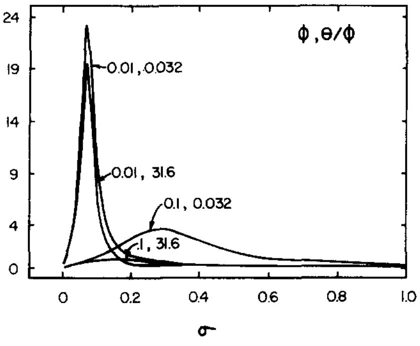

FIG. 1. Integrand $I(\theta, \phi; \sigma)$ vs σ for several values of θ/ϕ and ϕ.

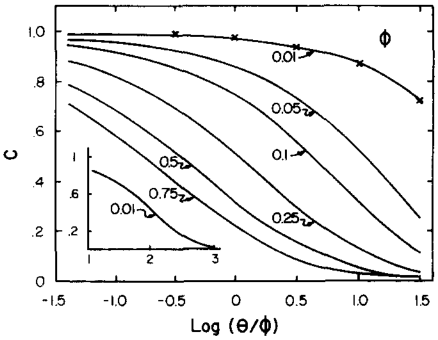

FIG. 2. Dimensionless concentration (C) profiles vs dimensionless time (θ/ϕ) for range of porosity values. Results from correlation (equation (6)) shown as *.

$$\phi \frac{\partial C}{\partial t} = D_{\text{eff}} \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C}{\partial r}\right). \tag{1}$$

While it is true that mass diffusion in the medium gives rise to a gradient in the partial pressure of the gas, pressure-driven gas flow resulting from this effect will generally be small when compared with diffusion.

The rate of diffusion of gas into the medium is exactly balanced by the time rate of change of bulk concentration in the isolated gas if the gas concentration there is uniform. This is normally true since sampling the gas for concentration measurement promotes mixing and ensures uniform properties. An equation for this balance is written as

$$\frac{\partial C}{\partial t} - \frac{2D_{\text{eff}}}{R} \frac{\partial C}{\partial r}\bigg|_{r=R} = 0 \tag{2}$$

which ensures a match of both concentration and mass flux between the isolated gas and porous medium at $r = R$. The boundary and initial conditions are

$$C(r \to \infty, t, \phi) = 0$$
$$C(r \leqslant R, t = 0, \phi) = 1$$
$$C(r > R, t = 0, \phi) = 0. \tag{3}$$

The thermal analog for this problem consists of transient conduction from a perfectly conducting cylinder of radius R and heat capacity $(\rho c)_1$ to a semi-infinite porous medium of effective heat capacity $(\rho c)_2$. An analytical solution is available [7]. The heat and mass transfer problems are analogous if D_{eff}/ϕ and 2ϕ are equated to the thermal diffusivity and α, respectively, in the solution of ref. [7]. The solution for the thermal problem is written in terms of mass transfer quantities as

$$C(\theta, \phi) = \int_0^{\infty} \frac{8\phi\, e^{-\sigma^2\theta/\phi}\, d\sigma}{\pi^2\sigma\{[\sigma J_0(\sigma) - 2\phi J_1(\sigma)]^2 + [\sigma Y_0(\sigma) - 2\phi Y_1(\sigma)]^2\}} \tag{4}$$

for $r = R$ which is of primary interest here. Both J and Y are Bessel functions of the first and second kinds and $\theta = tD_{\text{eff}}/R^2$.

SOLUTION

Discussion

The integrand in equation (4), written as $I(\theta, \phi; \sigma)$, is plotted against σ for fixed values of ϕ and θ (Fig. 1). Several points are noteworthy. All curves possess relatively large and narrow peaks which occur at small σ. The peaks become larger and steeper as porosity and time decrease, and occur at decreasing values of σ as $\theta \to \infty$ and $\phi \to 0$. Following the peak on each curve is an infinitely long 'tail' which approaches zero in this limit.

Obviously, analytical integration of equation (4) is not possible, and efficient numerical integration of it poses a small challenge. Fifteen-point Laguerre quadrature was unsuccessful. Newton–Cotes closed integration formulas work well in theory but are inefficient for integrating the tail. The small step size needed to accurately integrate in the neighborhood of the peak wastes computer time when applied to the tail. If ϕ is large enough so that much of the tail encompasses large values of σ, the integral in equation (4) may be written as

$$C(\theta, \phi) = \int_0^b I(\theta, \phi; \sigma)\, d\sigma - \frac{2}{\pi}\sqrt{(\theta\phi)} \sum_{k=0}^{\infty} \frac{(-1)^k(\theta b^2/\phi)^{k-1/2}}{(k-1/2)k!} \tag{5}$$

obtained by writing the Bessel functions of $I(\theta, \phi; \sigma)$ for large arguments and by using a series expansion for the exponential. In equation (5), b is a pure number large enough to justify large-argument approximations for the Bessel functions and the integral is evaluated using a closed integration formula. As $\phi \to 1$, equation (5) is useful since values of σ much greater than b normally occur in the integral of equation (4).

Integration scheme

Integration of $I(\theta, \phi; \sigma)$ was carried out using the trapezoidal rule with an *ad hoc* scheme for increasing step size in the region of the tail. The scheme maintains a small step size in those regions where $I(\theta, \phi; \sigma)$ is either increasing, peaking, or rapidly decreasing and increases the step size in the region where $I(\theta, \phi; \sigma)$ is changing slowly. Integration was rapid compared with a Newton–Cotes method and results obtained agree exactly with those of ref. [7] for porosity values of 0.25 and 0.50.

RESULTS

Profiles of dimensionless concentration of the isolated gas as a function of θ/ϕ and with ϕ as a parameter are shown in Fig. 2. The range of ϕ for this study was taken to be from 0.01 to 0.75. For small porosity, a small time rate of concentration change occurs at small θ/ϕ (in Fig. 2 this is most evident for a porosity of 0.01 but is true for other small porosities as well). This arises from a relatively small surface area for diffusion at small values of $\theta \ll \phi$. In the limit $\theta \to 0$, this is just the surface area of the well enclosing the initially isolated gas.

For moderate ϕ and θ, the time rate of change of concentration increases. This is because the area for diffusion has grown owing to the larger penetration depth of the diffused gas in combination with the fact that the con-

Table 1. Values for coefficients a_k in equation (6)

	k							
Φ	0	1	2	3	4	5	6	7
0.01	3.6222	−20.849	180.57	−865.36	2252.8	−3213.1	2355.9	−694.47
0.05	9.8206	−84.492	330.06	−628.21	573.49	−202.72	0	0
0.10	2.4084	−12.404	51.872	−120.70	132.29	−55.723	0	0
0.25	1.6622	−6.6183	11.758	−10.990	1.9871	0	0	0
0.50	1.6482	−14.661	64.760	−160.45	187.09	−83.448	0	0
0.75	1.7200	−28.813	268.40	−1489.8	4625.7	−8011.1	7219.5	−2636.7

centration of the gas continues to be relatively high at this time. At still larger values of θ/ϕ, concentration changes are slow as steady state is approached. This case corresponds to either large θ or alternatively small ϕ for which there is significant resistance to storage of gas in the medium (see equation (1)).

For porosity larger than 0.10, the diffusion process takes place over a time span of about $\theta/\phi = 32$ or less. For a porosity of 0.01 and smaller however, the span increases considerably to a minimum of $\theta/\phi = 1000$ as shown by the insert in Fig. 2. These results are useful when scheduling gas-sampling intervals for a test to determine *in situ* effective mass diffusivity. In this situation, diffusivity from laboratory tests can be used to calculate dimensional time from θ/ϕ (i.e. $t = R^2\theta/\phi D_{\mathrm{eff}}$).

Results of Fig. 2 were successfully fit to a polynomial

$$D_{\mathrm{eff}} = \frac{\phi R^2}{t} 10^{\sum_{k=0}^{7} a_k C^k} \tag{6}$$

where the coefficients a_k are presented in Table 1. For porosity other than 0.01, the correlations are valid for the range $-1.5 \leqslant \log(\theta/\phi) \leqslant 1.5$. For $\phi = 0.01$, the range is $-0.5 \leqslant \log(\theta/\phi) \leqslant 3.0$. Agreement between numerical results and the correlations was excellent, yielding a standard deviation of 0.01 or less in most cases. Results from the correlation for $\phi = 0.01$, shown in Fig. 2, are typical and provide evidence of the good agreement.

The utility of equation (6) is described as follows. Concentration data, C, and corresponding dimensional times, t, are substituted into equation (6) to produce an ensemble of estimated values for effective mass diffusivity. Some of the values of D_{eff} will normally be out of the range of applicability of the correlation used. The values of D_{eff} in this category will be inconsistent and sporadic, and should be ignored. Once consistence among D_{eff} for consecutive times is established, an average of these can be taken with the results being the desired diffusivity.

CONCLUSIONS

The thermal analog for mass diffusion of a gas in a semi-infinite porous medium has been used in a newly developed method to determine *in situ* effective gas diffusivity. The method uses correlations of results obtained by numerically integrating an existing solution for the thermal problem. Compared with the graphical results of Fig. 2, the correlations are simple, convenient to use (they are easily programmed on a hand-held calculator) and, as with the results of Fig. 2, are accurate for a broad range of porosity and time. With concentration time-history data, the method developed in this note eliminates the need for more-elaborate numerical models of mass diffusion when estimating *in situ* diffusivity.

The method may also be applied in the laboratory to measure effective mass diffusivities of materials such as cellular insulation [4]. For planar instead of radial geometries, the procedures of ref. [8] can be employed in a manner similar to the above.

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